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Photocatalytics Research Summary

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Photocatalytics Research

Over the course of the month that I have spent interning at the Chinese Academy of Sciences, specifically their branch of advanced applied physics, I have delved deep into research and learning with regards to the nature, functionality, and applications of photocatalysis and photocatalytic reactions. From the beginning of the month, I began gathering understanding and foundational knowledge of photocatalysis, as it was necessary to understand the field of research. I began by reading and studying numerous different publications and research papers regarding the topic, beginning with the basic functions of photocatalysts, their potential applications, and how they worked on the atomic level, building up my background understanding before delving into hyper specific methods of improving their photocatalytic potential and ability, and then finally participating in numerous practical testing processes and experiments.

The basic functions of photocatalysis rely on a light-based reaction that occurs within certain element combinations, specifically, the basis of photocatalysis is the migration of valence band electrons to the conduction

band of a given photocatalytic molecule or particle. The movement of electrons create opportunities for reduction and oxidation of reactants surrounding the photocatalyst, creating an environment in which both production of usable hydrogen as well as the degradation of organic waste is possible. From here, we infer the main goals of research and development of photocatalysts, energy production, and waste degradation. When a photocatalyst is submerged or mixed with water or otherwise exposed to a potential reactant, then exposed to certain types of light (which vary depending on the photocatalyst itself), the electrons within the valence band are excited, and migrate from the valence band to the conduction band. This leaves electron holes in the valence band, which are then able to oxidize the surrounding reactants, whilst the migration of the electrons themselves create the opportunity for reduction of surrounding reactants. When this occurs within water, the bonds between he hydrogen and oxygen are broken, and the H+ ions are reduced into H2, a usable form of hydrogen, whereas the oxygen, being the other remaining reactant, is oxidized into O2. This is the basic breakdown of energy production photocatalysis. On the flipside, the use of photocatalysis in reactants other than water provide a gateway to waste degradation. The process is largely the same, where the photocatalyst is submerged or exposed to the desired reactant, but in this instance, instead of pure water, it is exposed to organic waste. The same process occurs, with he migration of the valence electrons to the conduction band, but rather than oxidizing and reducing pure water,

it oxidizes and reduces organic waste. This essentially results in the creation of numerous usable products, such as H2O, CO2, or various organic acid such as OH radicals, essentially creating an avenue for waste reduction.

Beyond the most basic applications of photocatalysis, I also learned quite a bit about the optimization of photocatalysts and manners in which to bolster the effectiveness of photocatalytic reactions. The baseline of measuring the efficiency of photocatalysts is surrounding a measurement called STH efficiency. Measured in a %, the STH efficiency is roughly representative of the amount of solar energy successfully converted into usable hydrogen energy. Whilst this number isn't wholistically representative of a photocatalysts' efficiency, it generally represents how useful and effective a photocatalyst is. It is represented by the equation

$STH=\frac{R_{H_2}*\triangle G_{RXN}}{P_{\sum ¿*S}*100\%¿}$. The improvement of this efficiency is entirely necessary in order to bring the idea of commercialization of photocatalytic technology to the table, and the potential methodologies of improving said efficiency are vast, which I have researched for a decent portion of during my time here. The most simplistic way of improving the efficiency of a photocatalyst beyond a more efficient combination of elements is through two methodologies that are relatively similar, co-catalyst loading and non-metal/metal doping. Both of which, are slightly different renditions of

adding other materials onto the photocatalyst itself. Co-catalyst loading is the strategic placement of certain foreign materials on the photocatalyst in order to improve charge separations or provide active sites for reduction reactions. They act as electron sinks/holes, directing the electrons that migrate during photocatalysis in certain directions to do certain things. Doping is relatively similar to co-catalyst loading, only it occurs on a wider scale in terms of the photocatalyst itself. It is less direct and controllable than co-catalyst loading, as it requires less strategic placement, working only to achieve things such as band length reduction, or the lowering of recombination rates, rather than guiding reactions in specific directions.

Upon mentioning “band length” reduction, we delve into another facet of the photocatalysts functionality. This is another integral part of the photocatalysts efficiency and functionality, being the literal distance between the valence band and conduction band. This distance is important for several reasons, but the primary reason being that the band length represents the amount of energy necessary to excite the electrons in the valence band and spur migration. The longer the valence band, the more energy required to excite. For instance, in the most commonly used photocatalyst, TiO_2, or titanium oxide, the band length is relatively large in comparison to other photocatalytic materials, meaning that visible light photons do not contain the requisite energy to excite the electrons into migration, meaning that the only type of light that can cause photocatalysis to occur in TiO_2 is UV light, or any light with similar amounts of energy

intensity. This means that certain photocatalytic materials can function under different light conditions and types. On the flipside, the greater the distance is between the valence and the conduction band, the greater reduction potential there is in the photocatalyst as a whole. The most commonly tested way of rectifying this potential source of error is through the creation of heterojunctions, which is essentially the combination of two semiconductor photocatalysts in a number of different ways. There are 3 major types, that being the S type, the Z type, and type II. The type II is the most simplistic of the two, wherein it combines two semiconductors, one with a large band gap and one with a short band gap, in an attempt to allow the photocatalyst to function under visible light, whilst still maintaining the same efficiency by retaining one semiconductor with a large band gap. The ideal functionality allows for the electrons in the shorter band gap semiconductor photocatalyst, let’s call it SPA, to excite under visible light, and travel instead to the large band gap semiconductor photocatalysts’ conduction gap, let’s call it SPB. The next type, Z-scheme heterojunctions, is largely the same as the type II, with the major difference between the two being the existence of a mediator element in the Z-scheme. The mediator element is placed between the two heterojunctions, acting as a means of guiding the valence electrons from SPA to SPB’s conduction band. This rectifies the problems found in the type II design, whilst being more expensive as a mediator element is required. The S-scheme heterojunction attempts to combine these two types, creating a more efficient

heterojunction whilst not requiring the expensive mediator element. It does so by using very specific element combinations, one of which is more efficient at oxidization and the other more efficient at reduction. The S-scheme works relatively the same way as both the Z-scheme and the type II heterojunction, simply doing so with greater overall efficiency. It does, however, come at the cost of requiring very specific element combinations, which limit its overall potential.

Beyond doping, co-catalyst loading, and heterojunctions, there is one more mainstream methodology of improving photocatalyst efficiency during my time interning here, that being facet and surface engineering. This methodology is the broadest of the 3, having numerous specific means of application, but they are all essentially based on the principle of increasing the photocatalyst's ability to absorb light, a pre-reactionary improvement to the photocatalyst rather than a post-reactionary one. Like human cells, photocatalysts also are able to functionally absorb light at greater efficiencies when the surface area to volume ratio of the photocatalyst itself is relatively high. This means that increasing the surface area of the photocatalyst whilst ensuring that the volume remains relatively the same is an applicable improvement to the photocatalyst itself. This can be done most simply through finding a photocatalytic element that naturally forms into a desirable shape. However, things such as the intentional introduction of defects, or the use of specific renditions of photocatalysts with certain facet designs are also means of improving the surface area to light ratio.

Both of which, are as simplistic as they sound, with the introduction of growth and formation defects being literally a method of altering the physical shape of the photocatalytic particles, and the use of certain facet designs being literally the use of differing photocatalyst versions. For instance, TiO2, has {010}, {101}, and {001} facet types, which all have varying degrees of efficiency in terms of light absorption, and the incorporation of certain nanocrystals on the surface of TiO2 itself can provide light amplification, thus increasing the light absorption of the photocatalyst. Alongside this, the incorporation of core- shell structures, in which the photocatalyst is surrounded by some sort of shell structure, is another means of creating a more efficient photocatalyst. The main reason behind this is due to the unique optical properties that the shell can provide, creating an avenue to greater light absorption, as well as the shell's ability to protect the photocatalyst itself from an affliction called photo-corrosion. Certain photocatalysts are inherently susceptible to photo-corrosion, a process in which the reactants do not interact with the electron holes fast enough, and the photocatalyst begins performing the oxidation reaction with itself, thus damaging the photocatalyst. The presence of the shell prevents this from happening, essentially reducing the chances of the photocatalyst oxidizing itself via the incorporation of non-corrosive photocatalytic materials within the shell itself.

Finally, the last portion of my research into photocatalytics was with regards to the means of observing and testing photocatalytic materials.

There are 4 main devices that are used to analyze photocatalysts, the X-ray diffraction device (XRD), the X-ray photoelectron spectroscope (XPS), the scanning electron microscope (SEM), and transmission electron microscope (TEM). All of these devices and the tests that go along with them are designed to analyze specific aspects of the photocatalyst, with varying levels of specificity. The XRD, the most basic of the tests, primarily serves to determine the literal crystal structure of the photocatalyst, meaning the crystal structure, composition, and facet orientation of the photocatalyst. The test involves placing the photocatalyst on the testing stage, which will then rotate in a 1:2 position ratio with an electron detector. Electrons will then be fired at the spinning sample and fly off of it, providing a mapping of the peaks of the crystallite structure, or the structure of the overall photocatalyst. This is then graphically represented by a computer program, then matched with a sample published in an ICDD database, giving you translatable measurements and other data regarding the structure of the photocatalyst. The next test is the XPS, or the X-ray photoelectron spectroscopy. This test functions similarly to the XRD, but with the primary difference of probing a few nanometers into the surface of the photocatalyst itself. Electrons are fired into the sample, probing into it, before ejecting electrons out of the sample. The primary function of this test is to determine the chemical composition of the photocatalyst present, as electrons eject from differing chemical sources at differing speeds. These ejected electrons are picked up by a scanner which then map out the structure and chemical

composition of the photocatalyst itself. The next test is the scanning electron microscopy, or the SEM test. This test involves the use of a scanning electron microscope and is primary used to provide a visual image of the structure of the photocatalyst. This is useful for determining whether any sort of changes, as well as the surface structure of the photocatalyst itself are desirable for performing photocatalysis or not. It functions as any scanning electron microscope would, via the placement of the sample into a vacuum, and then firing electrons at the sample to “scan” the surface of it, providing an image on a computer that can then be analyzed. Finally, the transmission electron microscopy. This test functions similarly to the SEM test, as it also makes use of an electron microscope. The primary difference between the two, however, is the depth to which the electron microscope “scans.” The TEM test fires electrons through the sample, allowing for a mapping of the internal atomic structure of the photocatalyst. This again, allows for a visual analysis of the photocatalyst, the conductor of the test can visually determine the usability of the photocatalyst, as well as determine whether or not any changes made to the atomic structure of the photocatalyst have been effectively implemented. The TEM test provides the largest possible zoom on the photocatalyst itself amongst these 4 tests.

Beyond the research and building of knowledge that I have done here during my internship, I have also participated in a number of practical, lab based experiments/activities during my time here. Those being the creation of TiO2 via hydrolysis of titanium butoxide, the analysis of photocatalysts

via XRD and SEM testing, and finally, performing photocatalysis. The first practical experiment/activity that I took part in was the production of TiO2 itself, via the hydrolysis of titanium butoxide. The process first required me to sterilize the beakers and other tools necessary to perform the hydrolysis. Next, I needed to mix the titanium butoxide with ethanol, as well as water, via a mixing device. The process involves first mixing the titanium butoxide with ethanol, letting it mix, before combining said mixture with an equal part of water, meaning that the amount of water and ethanol present in the overall mixture is the same. I then set up a pressurized drip filter, via placing a porous film above a large beaker, and then attaching the drip filter to the top. The solution of titanium butoxide, water, and ethanol is then slowly poured into the filter's receptacle, adding only a portion at a time. The pressurized filter will begin filtering out the liquid portions of the mixture very slowly over the course of a few hours. Every 15-20 minutes or so I would return to the device and stir it up, scraping the unpurified TiO2 off the surface of the filter such that it would not clog. After filtering the entire solution, about 2 grams of unpurified TiO2 were left over, these would then be freeze-dried for approximately 24 hours. After drying, the unpurified TiO2 is taken to a small kiln, where it is fired at extremely high heat in order to remove all impurities. The final, leftover product is a couple grams of usable TiO2. The second of the practical experiments I took part in was an XRD and SEM analysis of a few different photocatalysts. The XRD was the simpler of the two, only requiring a sample of photocatalyst to be

placed into the device, having me start the test itself, and then merely watch as the data was graphed onto the computer program. The SEM test, however, required significantly more effort and work. The SEM test begins with sample preparation. There is a sample stage in the shape of a small circular platform. First, nonconductive adhesive must be placed on the sample stage, in small squares in order to differentiate the location of the samples, as well as which samples are which. The stage fits around 7-8 samples at a time, the application of the adhesive must be done meticulously, with tweezers, as other contact with the stage itself could interfere with the testing. Once the adhesive is applied, a toothpick is used to smudge a small bit of each sample photocatalyst onto the adhesive squares, the stage is then placed on the SEM's entrance. Given that the SEM test must occur within a vacuum, the stage is placed through an airlock before actually reaching the testing chamber. Upon reaching the testing chamber, the imaging process begins, and the stage is made visible on the computer screen. From there, the controls are used to operate the device, moving the focal point of the microscope from place to place, zooming in on the photocatalyst itself to map out its physical structure. Nearly all observations are recorded via a screenshot image, which is then saved to a specific file path. A new file path is created for each testing process, with subsequent file paths for each photocatalyst analyzed. Once all have been recorded, the test ends. The SEM is shut down, the sample stage returns through the same airlock and the data/images recorded are

burned into a CD disk, such that both hardcopy and digital data can be saved, as well as transferred. The adhesive squares are then removed from the sample stage and then thrown away. During the SEM testing I participated in, I observed numerous different unique photocatalyst structures, some of which, based on my research, would be more desirable than others for photocatalytic processes. I observed photocatalysts with rectangular shapes, circular shapes, ones with a large number of folds, as well as ones that were shaped similarly to tea leaves upon observation. The experience overall was incredibly interesting, as I had never experienced a testing process like that before. Finally, the last practical experiment I participated in was actually carrying out photocatalytic reactions using TiO_2. The process first begins with preparing a reactant solution, which includes the TiO_2. First, I ground up the TiO_2 powder using a pestle, mixing it with small amounts of ethanol whilst grinding it up. Afterwards, you repeat the same process with methanol, only difference being that the amount of methanol used is significantly greater than the amount of ethanol used. Continue grinding the powder and pouring what is left over into a solution. Once the solution is prepared, it consists of your photocatalyst, in this case TiO_2, a small amount of ethanol, and a large amount of methanol. Following this, the solution is placed into a special beaker designed for the photocatalysis testing device, it has two angled tubes that extrude out of its sides, which latch onto specific receptacles on the machine. The tubes and their receptacles are sealed with vacuum paste, allowing no interference

with the testing. The beaker itself contains a mixing magnet and is placed on a mixing stand as well and includes a cap that is designed to vacuum seal the beaker. Next, the vacuum is created, using the photocatalysis testing device, a pressurized filter removes the air from the device, ensuring that the reactions occur without interference within the vacuum. Finally, a light is placed on the top of the beaker, specifically on top of its glass cap, and shines the desired form of light upon the photocatalytic mixture. The testing essentially begins like this, as photocatalysis occurs over a period of time as the light is shone on the mixture, from here, you let the reactions play out for about an hour or so. The rate of photocatalysis is measured throughout the testing process via a computer program, which then displays the data on screen. Specifically, the data is represented through total amount of product produced over a certain period of time, essentially your typical XY plane graphical representation. Over the course of the photocatalysis I performed, the STH was roughly 2.2%, which is typical for baseline TiO2, and the total amount of product produced was roughly 3000 units an hour, over the course of 4 hours. I found the overall testing process incredibly interesting.

Over the course of the month I believe I have gained a concrete and practical understand of photocatalysis alongside all of the nuances that are involved within the topic. I have learned about the theoretical chemistry and physics surrounding photocatalytic processes as a whole, developed an understanding of the practical analysis of photocatalytic processes, as well

as studied the numerous methodologies applied to the improvement of photocatalytic processes. On top of all of this, I was able to apply my knowledge, albeit at a reduced capacity, in a real lab setting, something that was incredibly interesting. I greatly appreciate the time I spent here and hope to either return to further increase my knowledge, or find applications of what I've learned in my other future endeavors.